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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C08B 31/18, 37/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/31145</b> <b>(43) International Publication Date:</b> 2 June 2000 (02.06.00)
<b>(21) International Application Number:</b> PCT/NL99/00726 <b>(22) International Filing Date:</b> 26 November 1999 (26.11.99) <b>(30) Priority Data:</b> 1010660 26 November 1998 (26.11.98) NL <b>(71) Applicant (for all designated States except US):</b> INSTI- TUUT VOOR AGROTECHNOLOGISCH ONDERZOEK (ATO-DLO) [NL/NL]; P.O. Box 17, NL-6700 AA Wageningen (NL). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> SIVASLIGIL, Dogan, Sahin [NL/NL]; Wouwermanstraat 139, NL-2525 KR Den Haag (NL). BOGAERT, Piet, Marc, Paul [BE/NL]; Nieuwe Maanderbuurtweg 31, NL-6717 An Ede (NL). SLAGHEK, Theodoor, Maximiliaan [NL/NL]; Schansweg 35, NL-3042 HT Rotterdam (NL). <b>(74) Agent:</b> DE BRUIJN, Leendert, C.; Nederlandsch Octrooibu- reau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>In English translation (filed in Dutch).</i>
<b>(54) Title:</b> PROCESS FOR OXIDISING STARCH  <b>(57) Abstract</b>  The viscosity of starch and other carbohydrates can be lowered inexpensively, rapidly and without residual streams by treatment with hydrogen peroxide and a catalyst, in particular an organic acid or acid anhydride. After carbohydrate, hydrogen peroxide and catalyst have been brought together, the material is, if necessary, pre-dried at a temperature below 60 °C and the dried material is then treated at a temperature of 80 - 140 °C. The lowered viscosity is stable.		

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## Process for oxidising starch

The invention relates to a process for lowering the viscosity of carbohydrates by oxidative degradation.

5 Starch must be subjected to a treatment to lower the viscosity before it can be used industrially. To this end the starch is generally subjected to oxidative treatment at elevated temperature (40-60 °C) in an alkaline medium. For example, if hypochlorite is used as oxidising agent at 40 °C, the reaction takes 4 - 15 hours. The disadvantage of this method is the amount of salt formed and the extensive degradation of starch, accompanied by  
10 incorporation of chlorine. According to DE 738909, virtually dry potato starch can be gelled by treatment with hydrogen peroxide at 45 °C for 6 hours. Such a treatment is suitable for the preparation of blancmange, but the viscosity is too high and not stable for other applications.

According to another method, hydrogen peroxide is used with a transition metal as  
15 catalyst. However, the catalyst, which is usually toxic, is difficult to remove afterwards, even with the use of compounds such as EDTA. A further disadvantage is the discolouration of the product.

US-A 5,362,868 discloses a method according to which the viscosity of (hydroxy-ethyl)starch is lowered by oxidation with a per-acid. The per-acid used is, for example,  
20 peroxysulphuric acid ( $\text{H}_2\text{SO}_5$ ) or peracetic acid. The peroxysulphuric acid has to be prepared in situ from hydrogen peroxide and sulphuric acid. The reactivity of peracetic acid is lower and leads to longer reaction times. It is also described in US-A 5,362,868 that reaction with hydrogen peroxide leads to unacceptable reaction times.

According to WO 97/31951 the viscosity of starch and other carbohydrates can be  
25 lowered by treatment with hydrogen peroxide in the presence of an acylated carbohydrate.

The aim of the invention is to provide a method for lowering the viscosity of starch and other carbohydrates using simple reagents, without the use of heavy metals and salt-forming reagents, and without organic by-products. In this context it is desirable that a stable viscosity is obtained, that is to say a stability which does not increase further at  
30 ambient temperature.

Said aim is achieved by means of a method wherein the carbohydrate is oxidised with hydrogen peroxide in the presence of a catalyst and, after it has been brought into contact with the hydrogen peroxide, the carbohydrate is, if necessary, dried at a temperature below 60 °C and is then treated at a temperature of 80 - 140 °C.

The process according to the invention is an inexpensive method with short reaction times and with low consumption of hydrogen peroxide, consumption being approximately 5 times as low as with the method according to WO 97/31951. There is also no salt burden or other waste stream worthy of mention. The method leads in high yield and with  
5 little loss to a soluble or dispersible carbohydrate, the solution or dispersion of which has a low and stable viscosity.

Any polysaccharide that is completely or partially soluble in water can be used as the carbohydrate that can be treated in accordance with the process according to the invention. Such polysaccharides include, firstly, starch and fractions and derivatives  
10 thereof, such as amylose, ethoxylated starch and carboxymethylstarch. Furthermore, the solubility of cellulose and chitin and derivatives thereof can be improved, or the viscosity thereof can be lowered, by means of the method according to the invention.

The quantity of hydrogen peroxide to be used is entirely dependent on the desired degree of oxidation. By virtue of the higher efficiency of the method according to the  
15 invention, a limited quantity of hydrogen peroxide can suffice. In general a solution of 0.1 - 20 % (m/m) hydrogen peroxide, preferably of 1 - 10 % (m/m), is used. Preferably the quantity and concentration of hydrogen peroxide taken is such that the carbohydrate does not dissolve to a significant extent and, in the case of starch, remains in granular form. The catalyst can be an organic acid, such as acetic acid, formic acid, propionic acid, lactic  
20 acid, oxalic acid, citric acid, succinic acid or an anhydride such as acetic anhydride, and in particular a cyclic anhydride of a dicarboxylic acid such as succinic anhydride, maleic anhydride or citraconic anhydride, or possibly a lactone or lactide. Phosphoric acid can also be used. The quantity of catalyst is, for example, 0.1 - 4 % (m/m), in particular 0.5 - 2 % (m/m), with respect to the carbohydrate.

25 After hydrogen peroxide and catalyst have been added and mixed, the undissolved carbohydrate is filtered off if necessary. The water content must not be too high for the following step. If the water content is more than 20 or 25 % (with respect to the mass of the carbohydrate and water), the carbohydrate is then dried. Drying is carried out at a temperature of at most 60, and in particular below 55 °C, down to, for example, ambient  
30 temperature, to a water content of at most 25 % (m/m), in particular of 15-20 % (m/m), with respect to the carbohydrate. In the case of starch, drying must be carried out under conditions such that the starch does not gelatinise or barely gelatinises. Drying drums can optionally be used for drying on a large scale.

The dried carbohydrate is then kept at a temperature above 80 °C, in particular

above 100 °C, up to about 140 °C, for a period of at least 10 minutes, in particular for a period of 1 - 10 hours, during which period the actual oxidation takes place. At higher temperature, for example 120 °C, use can be made of fluidised beds, microwave ovens and the like. It is important that an open reactor is used, so that any residual water released can be removed easily. If the residual water is not adequately removed, the carbohydrate, in the case of starch, can then still gelatinise.

The viscosity of the carbohydrate of reduced viscosity that is obtained using the method according to the invention can be determined using a Brabender viscometer. According to the measurement method, a 25 % (m/m) solution or suspension is heated from 40 °C at a rate of 1.5 °C/min; during this heating the viscosity initially rises to a maximum (peak viscosity); on further heating the viscosity falls again; at 90 °C the temperature is not raised further and the viscosity reaches a minimum (valley viscosity); after 30 min at 90 °C cooling is carried out, again at a rate of 1.5 °C/min, to a final temperature of 40 °C; the viscosity at this end point is termed the final viscosity. The product according to the invention preferably has a peak, valley and final viscosity of 4,000, 200 and 2,000, respectively, with 2,000, 100 and 500 Brabender units, respectively, being most preferred, with a minimal reduction in the molecular weight. The product of reduced viscosity can serve as the basis for various applications. One important application is in paper making, where it can be used to increase the initial wet strength of the paper and to obtain improved printability, better adhesion of cationic agents and improved reception of adhesive.

#### Example 1

A quantity of potato starch (100 - 1000 g) is suspended in a solution of 5 % or 2.5 % hydrogen peroxide in water. Acetic acid or maleic anhydride is optionally added. After filtration, the material filtered off contains 30-40 % water; the hydrogen peroxide content is therefore about 1 % (m/m) at 2.5 % H<sub>2</sub>O<sub>2</sub>. The filter cake is dried in air for three days. Instead of this it is also possible to dry for a few hours under a stream of air at approximately 50 °C. The powder obtained is then kept at 120 °C in an oven for a number of hours (reaction time). The material obtained is white and has retained its granular structure. The number of carboxylic acid groups is approximately 1 per 57 anhydroglucose units. Brabender curves were recorded for the materials (25 % in water) at pH 7.0. The results are summarised in the following table.

Table 1

Reaction time	Catalyst		H <sub>2</sub> O <sub>2</sub>	Viscosity		
(h)	Type <sup>1</sup>	% <sup>2</sup>	% <sup>2</sup>	Peak	Valley	Final
3	AA	1	5	320	40	100
3	-	-	2.5	5480	300	7080
3	AA	1	-	<sup>3</sup>		<sup>3</sup>
3	AA	1	2.5	3760	148	3400
4	AA	1	2.5	3160	132	2680
3	AA+MA	1+1	2.5	32	32	32
3	MA	0.5	2.5	1010	40	98 <sup>4</sup>
3 <sup>5</sup>	MA	0.5	2.5	850	64	104

<sup>1</sup> AA = acetic acid; MA = maleic anhydride

5 <sup>2</sup> percentage by weight in water

<sup>3</sup> viscosity too high to be able to be measured

<sup>4</sup> after 30 minutes at 40 °C: 108

<sup>5</sup> wheat starch

## 10 Example 2

A quantity of potato starch (100 - 1000 g) is dried to a moisture content of at most 10 %. 2.5 % H<sub>2</sub>O<sub>2</sub> (2.5 gram per 100 gram dry starch, 100 % solids), 1 % or 0.5 % or 0.25 % acetic acid (with respect to dry starch) and 1.0 % or 0.5 % maleic anhydride (with respect to dry starch) are then added to the starch. The peroxide, acetic acid and maleic anhydride are all dissolved in water. The total quantity of water (water already present in the starch plus water added via the chemicals) is, however, no greater than 20 % (solids content of 80 %). The whole is mixed well in order then to react for 3 hours at 120 °C. The material obtained is white and has retained its granular structure. Brabender curves were recorded for the materials (25 % in water) at pH 7.0. The results are given in Table 20 2 below.

Table 2

Quantity of water (%)	Catalyst			Viscosity		
	H <sub>2</sub> O <sub>2</sub> (%)	AA(%)	MA(%)	Peak	Valley	Final
20	2.5	1	0.5	367	9	500
6	1.0	0.5	0.5	501	16	480
16	1.0	0.5	1.0	610	6	250(S)

S = Stable

## Claims

1. A process for lowering the viscosity of polymer carbohydrates by treatment with hydrogen peroxide in the presence of a catalyst, characterised in that the carbohydrate is brought into contact with the hydrogen peroxide and the catalyst and then, if necessary, dried at a temperature below 60 °C to a water content of at most 25 %, and the dried carbohydrate is treated at a temperature of 80-140 °C.
2. A process according to Claim 1, wherein the carbohydrate is brought into contact with a solution of 0.1-20 % (m/m), in particular 1-10 % (m/m), hydrogen peroxide.
3. A process according to Claim 1 or 2, wherein the catalyst is an organic acid, an organic acid anhydride or phosphoric acid.
4. A process according to Claim 3, wherein the catalyst is an anhydride of an organic dicarboxylic acid.
5. A process according to one of Claims 1 - 4, wherein the carbohydrate is dried to a water content of 10-20 % (m/m), with respect to the total of carbohydrate and water.
6. A process according to one of Claims 1- 5, wherein drying is carried out at a temperature of 20 - 55 °C and treatment is then carried out at a temperature of 100 - 130 °C.
7. A process according to one of Claims 1 - 6, wherein the carbohydrate is starch.
8. A process according to Claim 7, wherein the average molecular weight is 0.2 - 1 MDa.
9. A process according to Claim 7 or 8, wherein the final viscosity rises by less than 100 %, in particular by less than 50 % (in Brabender units) within one hour of completion of gelatination, at 40 °C.





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IPC 7 C08B31/18 C08B37/00

**B. FIELDS SEARCHED**

IPC 7 C08B

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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☒ Patent family members are listed in annex.

**"a" document member of the same patent family**

**15/03/2000**

**Mazet, J-F**

# INTERNATIONAL SEARCH REPORT

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